

Analysis of Hydrocarbon Vapor Probe Data

Red Hill Fuel Tanks

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Introduction

At the request of DOH staff, I have reviewed the monitoring data recovered from vapor probes installed below the Red Hill Bulk Fuel Storage tanks. In the review of the vapor data I will be:

- Evaluating the currently employed sampling and analysis protocols that are employed in conducting the soil vapor hydrocarbon analysis and making recommendations on the installation of the probes and changes in sampling and interpretive protocols that will improve the utility of these measurements;
- analyzing the changes in reported vapor concentration data among the full suite of vapor probes for their responses to known fuel releases;
- evaluating changes that may be occurring in response to environmental variables as well as other possible influences;
- assessing the value of the measurements in the context of early warning of new releases;
- making recommendations as to alternative monitoring protocols that may offer advantages over the current approach.

In light of the fact that I am working with incomplete information on the details of the exact methods applied in the field while making these measurements, my recommendations are provisional pending more information on those methods.

Background

The stated purpose of the soil vapor monitoring program is to detect evidence of leakage of stored fuels from the RHBFSF as early in the process as possible. The underlying theory is that, in the absence of leaked fuel, the hydrocarbon content of soil gases should be at negligible concentrations but, after a release occurs, fuel leaked through the steel tank walls will migrate through cracks and pores in the reinforced concrete encasement and migrate into the vadose (unsaturated) zone where it will descend through the porous basalts toward the underlying groundwater. As the fuel enters the vadose zone, the more volatile constituents will vaporize and disperse through the open pore space of the basalt lava flows that make up the interior of Red Hill Ridge. Larger amounts of released fuel would be expected to lead to higher initial concentrations of hydrocarbons, whereas smaller volumes would yield lower and less persistent concentrations of volatile hydrocarbons. Over time, the composition of the vapor phase would change as the more volatile constituents become depleted from the liquid phase and biodegradation removes the more easily consumed (light, short-chained) constituents. These processes, as well as dispersal would also be expected to reduce the overall hydrocarbon

concentrations but, as will be discussed later, other processes could reverse that trend for short periods of time

In order to detect changes in hydrocarbon vapor concentrations, suites of three vadose-zone vapor sampling probes were installed beneath the active tanks used at the Red Hill Bulk Fuel Storage Facility (RHBFSF) during the 2007 – 2008 timeframe and have been sampled on approximately a monthly basis since that time. The probes are configured as shown in Figure 1: three 0.1250" diameter soft copper (or stainless steel) tubes are nested inside a 3.5" diameter borehole, inclined downward at 15° from horizontal, with the tubes running down the inclined bore for distances of 25', 60', and 95' respectively. The three insertion distances are intended to monitor for vapor from infiltrating fuel at the inner edge (closest to the tunnel wall) of the tank, at the middle of the tank, and at the outer edge of the tank (hereinafter designated as shallow, middle, and deep probes); the bottom 10' of each tube is perforated with 3/16" holes, at 2' intervals, for vapor sample intake; each probe intake is isolated from its neighboring probe by a 7' plug of bentonite; the depth of open interval below the bottom of the steel tank base for each probe is estimated at 26.5' (for the shallow probe), 35.5' (for the middle probe), and 44.5' (for the deep probe).

It is my understanding that probe sets were installed beneath all 20 tanks; however, the data set that I have been provided omits data from any probes beneath Tank 1 and Tank 19; likewise, data is missing for the entire monitoring interval for the deep probe beneath Tank 6; the shallow probe beneath Tank 11; and other individual probes have extended periods of no values reported. Some of the latter gaps in data, reportedly, occurred during periods when the tanks were out of service for maintenance; and some for periods during which the probe lines may have been inoperable. In general, for those probes for which data are reported, the sampling interval appears to be approximately monthly but, during early sampling (prior to 2013) variations of as much as two to three weeks from that monthly interval are present; since 2013, the sampling is more regular except for the period immediately after the December 2013 fuel release when more frequent sampling was done for some of the probe sets close to Tank 5.

Sampling Procedure

The samples are withdrawn from each probe and analyzed using a hand-held organic vapor photo-ionization detector (PID) instrument capable of detecting organic vapors down to 1 part per billion (ppb) (see attached product literature). It should be noted that this instrument is only able to determine the presence and an approximate concentration of organic vapors (approximate because different organic compounds are more or less susceptible to ionization); it is not able to provide information on the composition of the organic vapor constituents. The PID is zeroed and calibrated with reagent gases containing a zero concentration and a known concentration of organic vapor at the start of each sampling day (this procedure has reportedly now been altered by the current contractor to multiple times during the sampling and analysis visit). Vendor literature claims a precision of 1 ppb when calibrated for a range from 1 to 9,999 ppb; 10 ppb for a range of 10,000 to 99,000 ppb; and 100 ppb for a range of 100,000 to 999,000 ppb. The instrument is able to pump ~500 cc/min of sample through the detector assembly.

Anecdotally, I have been told (by HM) that the probe lines are cleared of stagnant vapor by pumping and discarding the pump exhaust. Samples for analysis are then withdrawn from the probe lines through flexible tubing that is attached to a Tedlar® bag and the bag is inflated by vacuum suction. The vapor samples are then pumped from the Tedlar® bag through the PID sensor by the instrument; three readings are taken and the values averaged to yield the reported value. DOH staff (HM) who has witnessed the sampling and analysis procedure have indicated that purging of the individual lines is done for a few minutes, but no specific volume of soil gas is withdrawn during that process; further, withdrawal of samples for analysis is also done for a set time period, but without regard to the volume of soil gas withdrawn. It is also my understanding that the flexible tubing and Tedlar® bags used for the sampling from each probe are stored on-site within the chamber housing the probe end valves.

Probable Deficiencies With Current Sampling Procedure

If the information I have been provided on the sampling and analysis procedure are accurate, I believe that there are a number of deficiencies in the procedures being used that have the potential to render the data less precise and less reliable than they could be.

1. According to the DOH witness (HM), some probes yield gas freely, some only with difficulty. The apparent randomness of the gas volumes removed during purging of the tubing, and collected for analysis from each probe, could result in both highly variable, and erroneous sample results. It should be recognized that different probes will respond to pumping differently: some probes may be mounted in highly permeable rock formations and others may be mounted in zones having much lower permeability. This will have several effects on both the pumped volumes as well as the vapor concentrations observed. In the less permeable formations, much lower volumes of gas will be withdrawn during a given pumping interval and, in the event of a significant rainfall event, the permeability may become even more limited until the rainfall recharge drains from the formation. Under low permeability conditions, if the attachment of the flexible tubing to the valve at the discharge end of the probe is not entirely secure, then there is also the possibility that ambient air is being drawn through the pump rather than soil vapors from the probe. Hence, as a result of the low permeability, the pumping interval may not actually clear the tubing of the stagnant ground gas and a completely unreliable result will be obtained. (A secondary effect of the low permeability is that, in the event of a future release, the probes mounted in less permeable formations may respond much more slowly than those in more permeable formations. Hence, a set of probes in more permeable formations may respond to a release sooner than those in less permeable rocks even though the latter are closer to the point of release.)

Recommendation: It is essential that the probe lines be checked to ensure that they are clear of obstructions and that samples are being drawn from the formation around the probe end. These probes have been in place for more than a decade; they are located in what is supposed to be a normally unsaturated zone. But there is evidence that some of the probes have become

clogged or obstructed by debris; which suggests that the cavities in which the probes have been mounted have been periodically flooded and possibly fouled by debris or drilling materials and, hence, are not drawing a representative sample of vapor from the formation. If it cannot be verified that the probe lines are clear, then those lines should be replaced.

Where serviceable lines are confirmed, a secure connection should be used to draw a measured volume of soil vapor from the installed vapor tubing before collection of a sample of gas for analysis. A secure connection can be achieved using stainless or Teflon Swagelok fittings. A test for tightness would be to partially evacuate the sample line with the terminal valve closed and a pressure transducer attached; if, vacuum is held in the line, then a secure connection has been made. Similarly, a fixed standard volume of soil vapor should be drawn from every probe each time the sampling program is executed to ensure consistency among the probes and consistency between the monthly sampling exercises. At the very minimum, the tubing for each probe should be purged of stagnant gas by pulling a known, measured volume of soil gas (equal to 2 to 3 times the tubing volume - nominally 18.29 cc/m of 0.25 in. diameter tubing and ~4 cc/m of 0.125 in. diameter tubing - from each probe line and only then collecting a measured volume of sample for analysis.

I would also recommend that a validation exercise be conducted in which soil gas is drawn from each probe at a fixed, constant rate, while the gases from the pump discharge are tested repeatedly to ascertain whether, and when, a consistent analytical result is achieved for that probe. This will ensure that interaction between the vapor phase in the formation with the tubing during transport to the surface will be minimized.

It was recommended by a DOH consultant (GDB) that pressures also be monitored and recorded during the pumping exercise to ensure that no anomalies are observed there as well.

2. There appears to be no, or inconsistent, instrument validation from one set of probes to the next... There should be a "zero gas" and "span gas" run prior to sampling from each set of probes. Only if the zero and span gases yield appropriate results, should sampling proceed. Further, if there is a high reading for any of the individual probes for a specific tank, then there should be a zero/baseline test done before the sample from the next probe is collected and analyzed.

3. The onsite storage method for the sample bags and flexible tubing has high potential for contamination of the stored equipment with hydrocarbon vapors - this could significantly impact the levels of hydrocarbon being detected. An incident reported by DOH staff (HM): there was a significant drop in the values reported for Tank 18, from ~7000 ppb to about 300 to 500 ppb for both active probes from the May to June (2019) sampling round that continued for subsequent samples. When he inquired about that change, he was told that the flexible tubing had been changed immediately prior to the start of the June sample collections. This gives strong credence to probable contamination of all the equipment stored on-site between sampling campaigns.

I would further note that, when examining the full suite of data for the tanks, there is a nearly universal pattern of significant changes in the reported values when there is a transition from one contractor to another. In the attached table, I show, in the far right column, the name of the contractor who was providing the analytical results; the results for each contractor's first suite of samples has been highlighted in bold. The "new" results from that sampling exercise shows deviations of as much as 400% from the prior sampling averages. In my opinion, such variances should not be occurring: although there is no way for me to know how the procedures may have varied with the new contractors, I can reasonably assume that the conditions at the intake point for the individual probes are unlikely to have changed solely because a new contractor is collecting the samples and, therefore, these deviations are largely the result of variances in the equipment used or the sample collection procedure.

Recommendation: At a minimum, each sample should be taken with tubing and a bag that are demonstrably free of contaminants – re-use of the bags and tubing should only be allowed if it can be demonstrated that they are not retaining contaminants from prior sampling exercises. If there is an over-riding reason that they have to be stored on site, then both the tubing and bag should be checked for background readings using a zero gas (fill the bag through the flex tubing with zero gas, and take a baseline reading prior to sample collection). If it cannot be demonstrated that this sampling procedure can be accomplished without impacting the results produced, then an alternative sampling protocol should be implemented that eliminates the tubing and bag procedure entirely. Given the variations noted above (associated with different contractors) it is recommended that the new procedure be thoroughly tested to ensure that it is imposing minimal artifacts on the readings produced and that each step in the process be detailed according to well defined conditions (volumes, rates, pressures, etc.) so that the procedure can be replicated in detail by new field technicians or new contractors.

4. The samples are collected on approximately a monthly interval. There has not, to my knowledge, been an effort to determine how the vapor concentrations may vary with time during the day, or from day to day. Research conducted on soil gas transport has shown that subsurface soil gas is impacted by a number of surface phenomena; research in Hawaii has shown that this is especially true in Hawaii's porous rocks. Chief among the possible effects are those associated with changing barometric pressure as well as the effects of wind speed across the Red Hill Ridge due to the Bernoulli effect. Diurnal changes in barometric pressure typically cause air to migrate into the exposed soil during rising barometric pressures and allows soil gas to expand out of the soil column during falling barometric pressure. This effect is likely to impact only the relatively near surface soil vapor concentrations. The longer term pressure variances caused by wind speed acting on Red Hill ridge are more likely to enhance or decrease air exchange deeper within the ridge. However, a more significant effect may be associated with the effects of changing pressures within the lower adit: it is my understanding that the air pressure is maintained at a value slightly below the outside barometric pressure and could, depending on the quality of the seal within the adit walls, significantly contribute to air/vapor

transport in the vicinity of the probe intakes. Changes in the relative vacuum within the adit due to operational changes could be expected to induce some variability in the soil vapor concentrations detected. (Another significant pathway for soil gas extraction from the subsurface is through the monitoring wells drawing soil vapor through the well screen above the water table but this is unlikely to significantly impact vapor concentrations at the probe inlets.)

As discussed later in this report, I strongly suspect that thermal advection of the ground gas is occurring as a result of biodegradation of hydrocarbons retained in the vadose zone from prior releases. It is likely that advective transport will, in turn, be impacted by rainfall events: post rainfall decreases in formation temperatures may be reflected in reduced advective transport; saturation of less permeable formation with groundwater may alter vapor phase transport paths; extended drought periods may enhance transport as a result of decreased saturation and increased temperatures.

Recommendation: Ideally, withdrawal of soil gas with the pump discharge being sampled by the ppb RAE 3000 instrument until a stable vapor reading is achieved may be a more reliable sampling and analysis method but would need to be carefully tested against current methods to ensure that reproducible data were being generated.

As recently discussed (11/25/2020), continuous monitoring (or permanent installation of a probe capable of higher frequency measurement) of vapor levels would provide much greater insight into how these effects are expressed in the vapor data. However, in order to recover the most value from the enhanced monitoring, it will need to be implemented carefully and should be undertaken in stages: continuous monitoring at the full suite of probes beneath an individual tank for a limited duration (1 – 2 weeks), followed by similar monitoring at several other tanks for limited durations would answer many questions about the impacts of operational and environmental changes.

5. Recently, with a change in the contractors providing the sampling and analysis services to the Navy, I have been informed that the contractor has modified the procedure to include efforts to clear the lines of obstructions by injecting compressed air into the sampling ports. Simultaneously, the data reported have shown substantially lower values and some readings of zero concentrations of hydrocarbon vapor. Given the unusual number of zero and extremely low readings, in the absence of other information to the contrary, it appears that the practice of clearing the vapor probe lines is having a substantial impact on the readings reported. It was reported (HM) that about 5 hours was allowed to elapse between the time of clearing the lines and the sampling and analysis process. If a substantial volume of air was injected through the lines, into the vapor space around the probe inlets, this may not be sufficient time for equilibrium to be re-established between the formation volatiles and the injected air volume.

Recommendation: If the probe lines are cleared using compressed air, I would recommend that a volume of at least several times that of the injected air be withdrawn before sampling OR a period of several days be allowed to elapse between clearing the lines and subsequent

sampling. If pumping is done, then withdrawal of air from the probe should be continued until a constant vapor reading is achieved; even then, the resulting analysis may not be directly comparable to prior sampling and analysis exercises where no air was injected into the probe lines.

Summary Recommendation on Procedure for Sampling and Analysis

Soil vapor sampling has the potential to serve as a very useful monitoring method to determine, at an early stage, when fuel has escaped the confines of the steel tank and its concrete encasement. In order for this process to best serve this purpose, care needs to be exercised to ensure that the analysis results are an accurate representation of the vapor concentrations in the formation below the tanks. Significant effort invested in the design of the current sampling procedure, to ensure that the results are accurate (and reproducible) for a given sampling episode, will allow the Navy to more reliably assess the condition of their tanks and to recognize, at an earlier stage of a release, that fuel is entering the vadose zone below the tanks. With that information they will be able to respond more quickly and more effectively to reduce the volume of the release and limit the impact of the release on the environment.

If continuous/more frequent monitoring is implemented at one or more probes, the data produced have the potential to allow the Navy to incorporate an understanding of the impacts of environmental (and operational) variables) into their analysis of the data to better recognize variances associated with fuel releases and to respond and manage those releases with as little impact on the environment as possible.

Interpretation and Analysis of prior Vapor Probe Data

In very general terms, the vapor concentration data recorded over the course of the monitoring program spans a significant range: the lowest concentrations recorded are in the single digits of parts per billion (and possibly as the detection limit of the instrument, if the zero readings are accepted at face value); the highest values recorded are as high as 450,000 ppb. This upper level value is likely to be, at best, a rough approximation of the levels due to instrument saturation. During the early years of monitoring, a number of elevated values were reported for the higher-number Tanks (10 and above) and fewer elevated vapor values found in the lower numbered tanks. Although possibly of historical interest, the elevated measurements in the upper storage facility are outside the scope of the current report and won't be dealt with in detail here.

Visualization of the Data: The focus of the current report will be on the release from Tank 5 and the data variations that may be associated with that event. However, a brief digression is needed in order to provide a context for understanding the data presentations that will be offered below. The data produced by the vapor monitoring program presents some challenges for analysis and visualization due to both the large size of the data set as well as the broad aerial extent of the sampling locations. Typically, time series data are presented as plots of measurement/amplitude values on the "Y" axis and time on the "X" axis (Figure 2). In Figure 2 are plotted the vapor concentration values (on a linear vertical axis) for the three vapor probes below both Tank 3 and Tank 5. Clearly, the very high values for Tank 5 after the December, 2013 release are clearly visible, but don't allow us to examine any details in the concentration values for Tank 3 beyond seeing that the deep probe below Tank 3 spikes somewhat after elevated values were seen below Tank 5. Plotting these same values on a logarithmic axis allows us to better visualize the changes in vapor concentrations below Tank 3, but heavily mutes concentration variations of less than a factor of ten. It's also clear that plotting more vapor probe data for more than two or three tanks will only yield a confusing cloud of lines and, hence, tracking the effects of the release on more distal subsurface vapor concentrations is, at best, difficult.

The concentration data for the entire tank installation can be plotted on what is called a "waterfall" plot (Figure 4, Hugh Meyers, personal communication). This plot allows visualization of the entire data set simultaneously, as a three-dimensional (3D) bar graph, and shows very quickly where very high vapor concentrations are occurring. The 2013 release at Tank 5 indicates the onset of extreme vapor concentrations and their later progressive decline; later high values, of short duration, are also evident at Tank 7, as well as smaller, but still elevated, values at Tanks 17 and 18. However, all bars are plotted on a single vertical axis scale and the very high values at any single site mutes the smaller variations in vapor concentration that occur in the surrounding vapor probes after the December 2013 release. Removing the values for Tank 5 vapor probes, Figure 5, does allow somewhat better visualization of the vapor increases in the adjoining tanks' probes, especially the extremely high values in the Tank 3 probe which occurs beginning in late January, 2014, and extending into March, 2014. It should

also be recognized that the time axis on these plots is not linear – the bar graphs for each probe are plotted in sequence whether samples were collected at daily intervals or monthly intervals and, hence, the apparently large data gaps are generated by the frequent sampling at and around Tank 5 while maintaining a monthly sampling interval for the more distal tanks.

A third approach to presenting the data is as a “heatmap” where values are presented as a matrix where each cell of the matrix is color coded according to the concentration of the vapor measured. We can apply this method globally to all of the data on the same color scale, or use the color scale on subsets of data so that we can more clearly see relative changes within a selected sequence of data. For the current analysis I have applied the color coding uniformly to the probes below each tank which yields the heat map in Figure 6. The values for the entire monitoring period are presented in Figure 6 with the data for each tank’s probes outlined with a black border; this figure also segregates the early vapor data, spanning March, 2008, through April, 2013, from the more recent data set beginning in May, 2013, through October, 2020. (Note that the cells without color are for dates when probes were not sampled due to malfunction of the probe or due to sampling of only a subset of probes on a particular date or where data are considered suspect.) This mode of presentation allows us to immediately identify significant deviations in vapor values within a given set of probes and to clearly see how, and when, probes below adjacent tanks are affected by those high vapor concentrations by significant increases above prior average values for that probe set. This approach also allows us to focus in on a specific time frame or subset of probes for a more detailed review of the specific values of vapor concentrations (Figures 7 and 8). A separate high resolution pdf is provided with the full data set to which the reader can refer for details of date and concentration values.

Data Analysis: For purposes of the present discussion, we will accept (nearly) all vapor values as accurate representations of the vapor phase concentration of hydrocarbons in the vadose zone below the tanks. The earlier discussion commenting on (what I understand to be) the methodology of sampling and analysis, as well as other factors that could potentially affect the vapor concentrations reported, indicates that this is not, in fact the case and, hence, conclusions drawn need to be considered in light of those cumulative uncertainties.

As noted previously, during the early years of monitoring, high vapor concentrations were found in samples recovered below the higher- numbered tanks; these show up quite clearly in the Figure 6 heatmap and are assumed to be associated with releases of varying volumes of fuel from one or more of the tanks in the upper part of the facility. The duration of the high vapor values sometimes lasted for several sampling intervals although there were also shorter episodes of high vapor values that occurred during a single month that had abated by the next sampling interval. By early 2013, the vapor values at the majority of the tanks were quite low.

Tank 5: Focusing initially on the probes below Tank 5, the values from May through November of 2013 were quite low, in the range of several tens to a few hundred ppb (see key #1, Figure 7); the average for those months for the shallow, middle and deep probes were 134 ppb, 163 ppb, and 189 ppb. In December, the values rose to 622 ppb and 794 ppb for the middle and

deep probes reflecting a roughly 400% increase above the prior average and, very likely, induced by fuel released during the refilling of Tank 5 that began on December 9, 2013. The shallow probe remained at low levels for this sample date and suggests that the discharge from the tank's concrete encasement was likely on the opposite side, away from the tunnel, and distant from the shallowest probe inlet. During the January 15th sampling episode the middle and deep probes for Tank 5 increased to ~300 times the prior averages whereas the shallow probe showed only a doubling in value. During subsequent sampling of Tank 5 probes showed a modest decrease from the initial peak vapor concentrations through mid-March (2014), but began increasing to a second peak in mid-April of nearly twice the initial peak seen immediately after the release. Hydrocarbon vapor concentrations remained at high levels into 2015 when the deeper values started to decline and the shallow values increased to levels ten times higher than those found in the middle and deep probes in 2016. Values have progressively declined since then, but have not yet reached levels as low as those present before the 2013 release.

The dual peaks in vapor concentrations may be associated with multiple pathways taken by the fuel after leaving the steel envelope as it migrated through the concrete encasement; we know that there were multiple leaks through the steel and there may have been multiple pathways through the concrete encasement of varying hydraulic conductivity and length. However, it should also be noted that Honolulu experienced varying rates of rainfall during the initial period following the release: some months experienced significant rainfall accumulations and other months having lower rainfall rates (monthly rainfall accumulations, in mm, are presented on the extreme right and left of the vapor data columns). A plausible mechanism for dispersal of the LNAPL within the vadose zone is a recharge event that flushes pooled LNAPL out of topographic depressions and spreads it further downslope; a much higher distribution and surface area of the LNAPL would lead to an increased rate of volatilization.

Another rainfall-related alternative that should be considered is the observation, noted in the Gammon report, that groundwater is able to infiltrate into the gap space between the steel and concrete encasement – and was discharged through the “tell-tale” lines that were installed to intercept leaking fuel (these lines were subsequently removed during tank maintenance work). Groundwater, after an intense rainfall event, could infiltrate into the gap space and flush out residual fuel that had escaped the steel tank, but had not yet been able to escape the concrete encasement, and drive that fuel into the underlying formations.

Outlying Tanks

The vapor concentrations from probes for the tanks adjacent to Tank 5 also show substantial responses to the 2013/2014 release:

Probes located below Tank 3, the closest to Tank 5, show an almost immediate increase in vapor concentrations, but that increase occurs only in the deepest probe, whereas the shallower probes show a more muted and delayed response. The increase in values beneath Tank 3 are much higher in the deepest probe (which were about ten times higher than any seen at probes below Tank 4, and nearly that multiple of values seen below the tanks up-slope of

Tank 5). I interpret this pattern to suggest that the high vapor values in the deep probe are the result of LNAPL migrating downward and down slope below the Tank 3 deep probe and suggests that the LNAPL may have reached the water table.

Tank 4, located next-closest to Tank 5, showed more modest increases at its probes than those at Tank 3 in the January 30 sampling exercise but did show sharp increases in the March 21, 2014 sampling that were contemporaneous with the highest value in the deep Tank 3 probe. The 3/21/2014 values were ~100 times higher than prior averages, but never approached the magnitude of the highest Tank 3 deep probe values. Also notable in the Tank 4 (3/21/2014) values is that we don't see as great a divergence between the deep and shallow probe values; this suggests that the LNAPL source for the vapors is likely located at a greater distance from these probes. There are also sharply elevated values below Tank 4 in the January and May (2015) sampling exercises that may be related to the 2013/2014 release; these will be discussed below.

Tank 2 probes, located farthest downslope of Tank 5, maintained low values through March, 2014, but showed values well above prior averages by May, 2014, and remained higher than previous averages through 2019 (with some occasional spikes to much higher values in 2015 that will be discussed below).

Probes for Tanks 6, 7, 8, and 9, located up-slope of Tank 5, also showed significant increases above their prior averages. These increases occurred nearly simultaneously with the initial high values at Tank 5 in mid-January, 2014. Initial values below Tank 6 were about 30 times lower (3%) than those at Tank 5 probes, but the values at the closer tanks gradually rose to ~10% of the Tank 5 levels over the next several weeks. The more distant tanks showed progressively lower concentrations, with increasing distance, relative to Tank 5 vapor levels, but vapor values at probes beneath Tanks 10 through 12 also appear to have been impacted by the release at Tank 5 with more modest increases in concentrations. The values beneath the upper tanks, with exceptions that will be discussed below, gradually decline toward their prior values and begin to reach levels similar to their averages prior to the 2013/2014 release by 2018.

Probes below Tanks 13 through 16, during this period also show significant vapor concentration increases as well. However, Tank 17 showed significant hydrocarbon vapor concentrations as early as 5/13/13 (prior to the Tank 5 release) and makes any attempt to interpret possible impacts of the Tank 5 release on vapor concentrations in this area of the tank farm problematic and will not be attempted.

Interpretation of Vapor Concentration Variations Subsequent to 2013/2014 Release

Although the observed behavior of the vapor concentrations is, at best, difficult to uniquely attribute to a specific set of circumstances within the vadose zone, there are plausible interpretations of the responses observed. The data from the probes below Tank 5 suggest the following:

1. Vapor values below Tank 5 began within days of the start of filling operations at Tank 5. Although the increased vapor concentrations were not extraordinary (within the context of variations seen within the entire data set), they were substantially higher than prior averages and occurred during a critical operation that was underway at Tank 5.

2. The increase in vapor concentrations was not monotonic: vapor values increased to an initial peak, then fell significantly before rising to their highest levels about five months after the tank filling operations began (and more than three months after the tank had been drained). This suggests that there were multiple release pathways (or mechanisms). One plausible explanation for the observed pattern is that residual fuel had accumulated between the inner steel envelop and the concrete encasement. Some of that fuel was released immediately, but the residual escaped after the bulk of the fuel had been drained from inside the steel tank. The distribution of the vapor concentrations is consistent with this: the initial high vapor value was observed in the deep/outer probe; the second peak in vapor concentrations showed about equal concentrations at the central/mid-depth and the deep/outer probe whereas the shallow/inner probe reaches concentrations no higher than half those of the other two. As noted above, the role of rainfall/groundwater in transporting and dispersing the released fuel is uncertain, but cannot be dismissed. The release occurred during a period of moderately high rainfall accumulations and, as noted previously, the Gammon report details observations of groundwater infiltrating the space between the steel tank walls and the concrete encasement. Further discussion of rainfall and its effects on vapor concentrations will be discussed below.

The vapor values observed in the tanks located lower than (southwest of) Tank 5 in Redhill Ridge are interpreted as follows:

3) Increased vapor concentrations were observed at the deep probe below Tank 3 very soon after high values were observed at Tank 5 (it is unfortunate that Tank 3 probes were not sampled simultaneously with those at Tank 5 on January 15, 2014; they might have further confirmed that a release was underway). Clearly there was gas phase transport of LNAPL volatiles from Tank 5 to the Tank 3 probes almost immediately after discharge into the vadose zone.

4) The Tank 3 deep probe continued to increase during the following two months and reached a value substantially higher than any concentration observed below other outlying tanks around Tank 5 and, in fact, exceeded the highest measured value below Tank 5 during that sampling round by more than 50%. These high values, as well as the strong gradient from the deep/outer probes to the shallow/inner probes, is interpreted to indicate that LNAPL flowed down the strike and dip of the lava flows within the ridge and passed in close proximity to, and below, the deeper probe. The apparently (here again, a more aggressive sampling program would have provided more definitive data) rapid fall-off in concentrations from that peak suggests that the LNAPL continued to migrate downward and out of range of the deeper Tank 3 probe.

5) As discussed below, a second factor in the rapid decline of vapor values below Tank 3 and its companions is attributed to active, thermally driven, gas phase transport through the ridge along the strike and dip of the lava beds. Thermally driven advective transport would be expected to draw less-volatile-rich air from downslope (the southwest end of the ridge) and carry it towards the northeast, up slope, toward the higher-numbered tanks.

6) Vapor values below Tanks 2 and 4 showed more modest, and more evenly distributed vapor concentrations that I attribute to gas phase transport and dispersion. Increases in concentration occur at Tank 4 relatively soon after elevated values appear below Tank 3 whereas Tank 2 shows a significant increase above prior values about three months after the release began. Here, again, there was not consistent sampling throughout the area and, hence, values may have been increasing below Tank 2 nearly a month earlier.

The vapor values observed in the tanks located higher than (east and northeast of) Tank 5 in Redhill Ridge are interpreted as follows:

7) The very rapid rise in vapor values below Tanks 6 through 10 (January 15 and 30, 2014) is strong evidence for vapor phase transport from the point of discharge into the vadose zone toward the NE. Although the initial rise in vapor concentrations below these tanks is rapid, the magnitude of the early values is modest (<7000 ppb at the highest). The second peak in concentrations at Tank 5, in March, 2014, is accompanied by vapor concentrations that were as much as six times higher than those seen previously at both the odd-numbered (directly up-ridge) and the even-numbered (across-ridge) tanks and suggest a much larger source of hydrocarbon volatiles. The distribution of concentrations also appears to be quite uniform, not showing a strong gradient from shallow (near tunnel) to deep (outside edge of the tanks); there is, however, a fairly strong gradient from between the odd- and even-numbered tanks with the latter showing values that are half or less than the values of their odd-numbered "partner" tank. The much higher larger source may reflect a release that reached the water table and spread over a much larger surface area for the fuel to be volatilized from. Although this hypothesis is by no means a unique explanation for the recorded values, it is consistent with them.

8) The great disparity in the vapor concentrations found below the tanks southwest of Tank 5 and those east and northeast (as much as fifty times higher in the northeast), is consistent with a strong advective flow of subsurface gases toward the northeast along the strike and dip of the lavas within the ridge. The temperature measurements made in the monitoring wells, as well as the orientation of higher and lower concentrations, suggest that this is thermally driven advective transport. (In the absence of a heat source, the addition of (most) hydrocarbon vapors will increase the density of an air mass resulting in downward flow – completely contrary to the observed data).

Short-term/episodic Vapor Concentration Variations

Within the entire data set there are a number of shorter term variations in vapor concentrations that are not associated with the Tank 5 release. I will not attempt to evaluate

the majority of them: some, where high values persist beneath a given tank for an extended period of time, can reasonably be inferred to be associated with a fuel release of some magnitude. Other, one-time, high value vapor readings, are more likely due to equipment malfunction (whether of the probes or the PID).

There are other sets of readings that are more problematic. We see an unusual pattern in the measurements made on 10/27/14, 1/28/15, and 5/28/15: all are associated with anomalously low values for most of the probes below tanks up-ridge from Tank 5. The 10/27/14 values in the tanks below Tank 5 are somewhat depressed compared to those before and after that date, but the values observed below Tanks 2 and 4 are substantially elevated (by a factors of as much as 10 or more) above the prior or following values for each probe. Whether these deviations are associated with instrument malfunction or with an environmental change (e.g. rainfall) is not at all clear. Rainfall accumulations during the months of the first two sets of anomalous values were quite high, and above average, respectively; the rainfall for the third set of data was normal to low.

Another set of data that stands out is the sampling round of 9/30/15: it too shows a one-time significant decrease in vapor concentrations below prior and following values, for the majority of the probes sampled. This suite of values is also associated with unusually high rainfall accumulations, but also correlates with a change in contractor from ESI to Element Environmental. During prior change-overs from one contractor to another, we see a similar (although not identical) pattern in decreasing values for the first one or two sampling rounds.

We can also see a sudden, continuing change in the values for Tank 18 beginning in June, 2019, when values decreased at the two functional probes, shallow and deep, from an average of ~5000 ppb to an average of ~500 to 800. This change, discussed in the review of the sampling protocols, occurred when, according to the contractor, the tubing used in the sampling process was changed.

Analysis

The above observations are significant, and worthy of examination, because the 2013/2014 release produced a small but significant (~4X) increase in vapor concentrations below Tank 5 within days of the time filling operations began; had the Navy been able to respond appropriately to those increases, the volume of fuel released, and potential for impacts to drinking water supplies, could have been reduced by an order of magnitude. However, the scale of variations that typically occur in the vapor data – that are not (likely) associated with a fuel release event – have much larger magnitudes than the changes that occurred during the early stages of the 2013/2014 release. If we can better understand the source of these variations, and, where possible, reduce or eliminate those associated with incorrect or imprecise field protocols, then this expensive and time consuming effort can better meet the objective of reducing fuel losses and reducing the impacts of those losses on the underlying groundwater.

A definitive analysis of the vapor variations associated with rainfall rates is challenging. As noted, there are a number of significant – if contradictory – variations associated with large monthly rainfall accumulations. That association is somewhat indirect: the changes in vapor concentrations don't usually occur during the month of high rainfall, but more typically a month or more after the peak rainfall accumulation. There are also episodes of large accumulations of rainfall that show only modest, or isolated, variations.

There are several plausible, if not unique, explanations for the observed vapor concentration responses to rainfall events. A significant rainfall event will result in sub-horizontal water flow along the strike and dip of the stratigraphy within Redhill Ridge; this behavior has been observed nearby in the open face of the Halawa Quarry where water will flow out of the clinker layers between the massive a'a interior units. As noted above, gas phase transport allows rapid movement of hydrocarbon vapors across substantial distances within the ridge. Introduction of large quantities of recharge water has the potential to saturate formations that were previously more open to vapor transport and effectively, and temporarily, "turn off" that long range transport of LNAPL volatiles. Alternatively, the driving force for that advective transport can plausibly be assigned to the thermal effects arising from biodegradation of residual LNAPL in the vadose zone: a significant rainfall recharge event could effectively cool the formation and, again, temporarily "turn off" the energy source for long distance transport of the volatiles.

The "contradictory" response, the significant increases in volatile vapor concentrations after large rainfall accumulation are, as discussed above, plausibly assigned to mobilization of residual or pooled LNAPL, either in the formation or within the tanks' encasements, out into the vadose zone where volatilization of the LNAPL will be detected by the vapor probes. This hypothesis is, to a degree, supported by the fact that an apparent association between rainfall and elevated values only occurs when there is other evidence for a prior release and only in proximity to that assumed release (e.g. in addition to the observations around Tank 5, Tank 18 shows elevated values from April 2014 through February 2015; higher than normal values are recorded below Tanks 14 through 16 in late May, which also experienced higher than normal rainfall). We note too, that since February, 2017, there hasn't been a month with a particularly large accumulation of rainfall and there have, likewise, been no clear evidence of significant reductions/increases having this pattern (with the possible exception of the most recent data when new sampling protocols were implemented).

Summary

I would summarize the important findings of the present analysis as follows:

- 1) Subsurface vapor concentrations respond very quickly to introduction of LNAPL into the vadose zone around the Red Hill tanks;
- 2) There is gas phase transport of LNAPL volatiles over significant distances within Red Hill Ridge. The most likely driving force for gas phase transport within the ridge is thermal advection driven by heat produced by biodegradation of residual LNAPL within the vadose zone or in the underlying groundwater (or both).;

- 3) In addition to the changes in vapor concentrations associated with fresh releases, there is significant variability in concentration values that is likely induced by a combination of environmental variables (rainfall, possibly wind driven pressure gradients, etc.), possible anthropogenic variables (pressure variations within the tunnels), and the interaction of these variables with long range advective transport.
- 4) In addition to the above interaction, there also appears to be interactions between rainfall recharge and pooling of LNAPL within the concrete encasement or in the basalt after the LNAPL is discharged from the steel tanks;
- 5) There is clear evidence of variability in the reported vapor concentrations related to the field procedures applied during the sampling and analysis campaigns.

Recommendations

- 1) The highest priority task is to conduct an audit of the field procedures to determine whether and where current sampling procedures are providing accurate, reliable, and reproducible analytical results representative of hydrocarbon vapor concentrations from the individual probes.
- 2) Where probe lines are malfunctioning or plugged, those probe lines, or probe sets, should be removed and replaced with functional probes.
- 3) An analysis, validation, and response procedure should be established that:
 - a. establishes a reasonable set of dynamic concentration thresholds for each probe (e.g. 500% increase above prior four-month average);
 - b. a process for resampling and re-analysis of vapor from probes that exceed those thresholds to confirm the relative exceedance (e.g. resampling 24/48/72 hours later);
 - c. an appropriate SOP if the elevated values are confirmed (e.g. continued close monitoring, tank tightness, or increased fuel level monitoring) or show a continuing/accelerating increase (e.g. begin preparations required for draining tank) in the absence of other factors that are known to yield anomalously high values.
- 4) Modify reporting procedures so that, in particular, anomalous vapor levels can be evaluated by trained, responsible individuals who are authorized to initiate appropriate actions when presented with evidence that a significant release may be underway.
- 5) If/when a continuous monitoring program is implemented, an integrated data set (probe location, apparent permeability around each probe, etc.) will need to be evaluated for environmental and anthropogenic impacts on vapor values as well as the varying characteristics of the stratigraphy within which the probes are mounted.

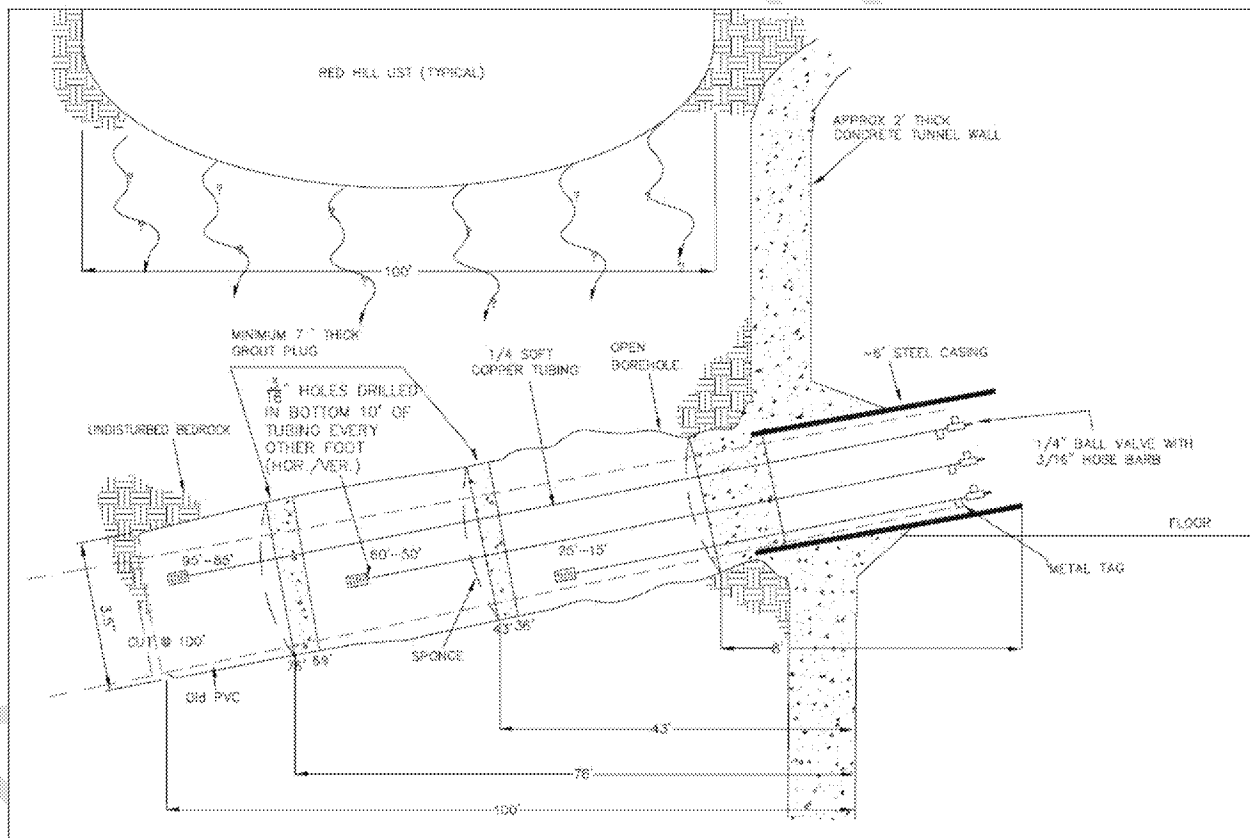


Figure 1. Schematic diagram of installation of soil vapor probes.

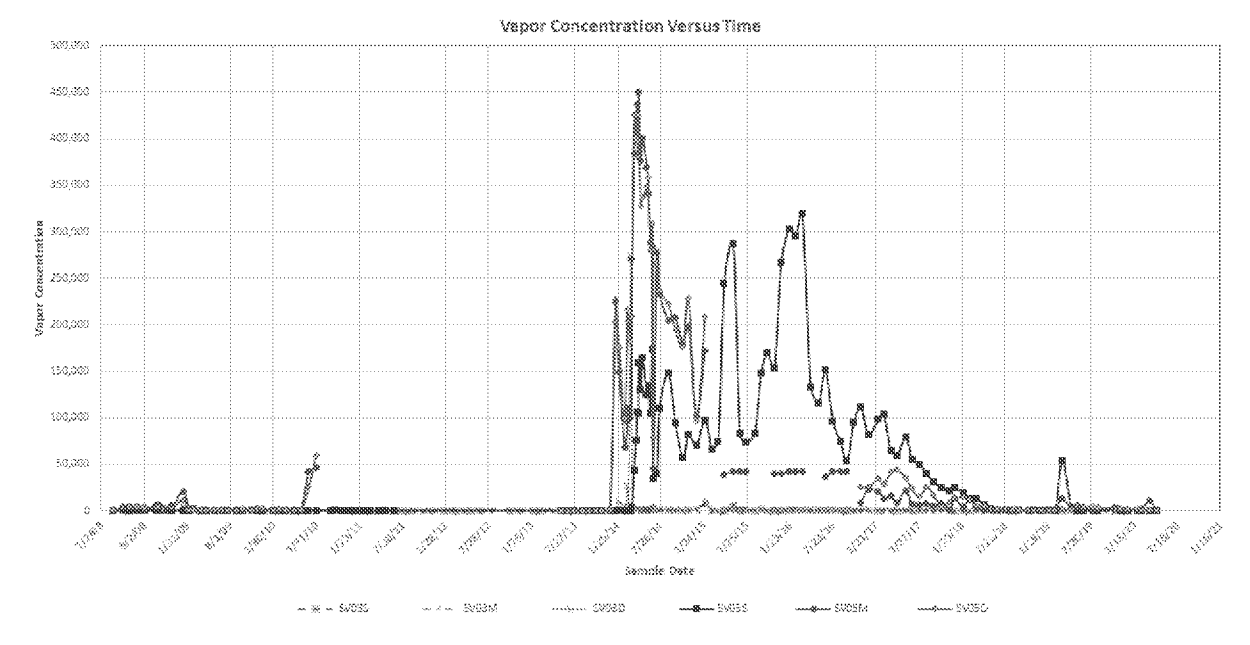


Figure 2. Concentration versus time on linear concentration axis

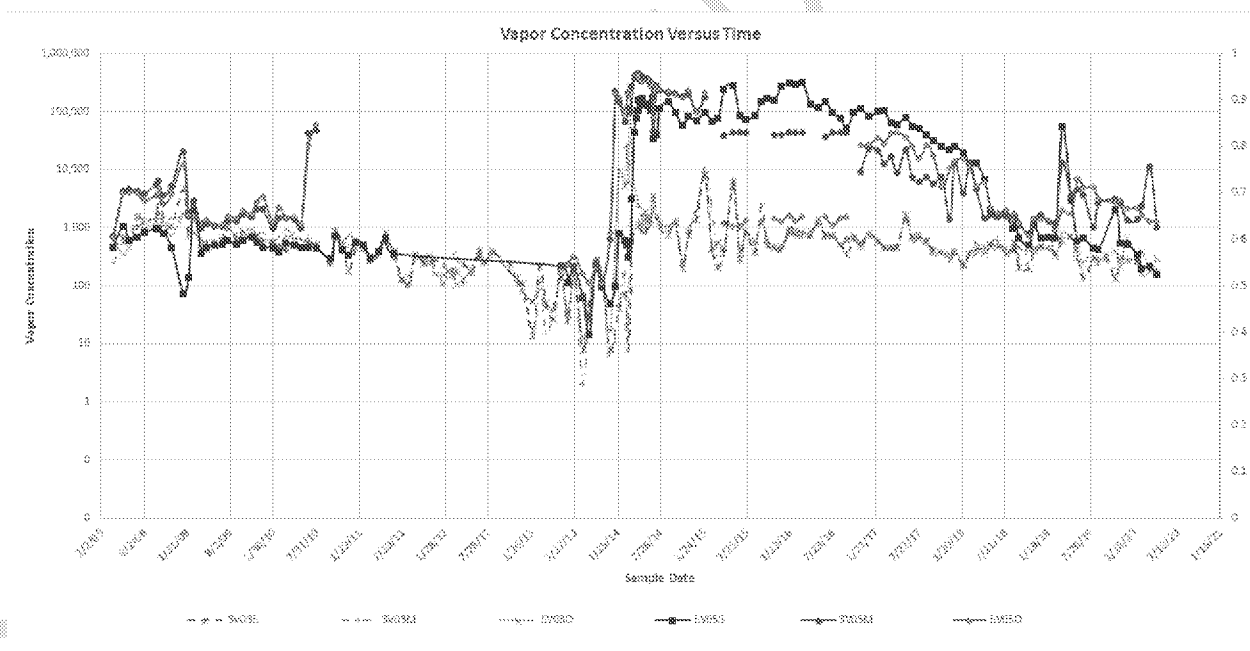


Figure 3. Concentration versus time on a logarithmic concentration axis

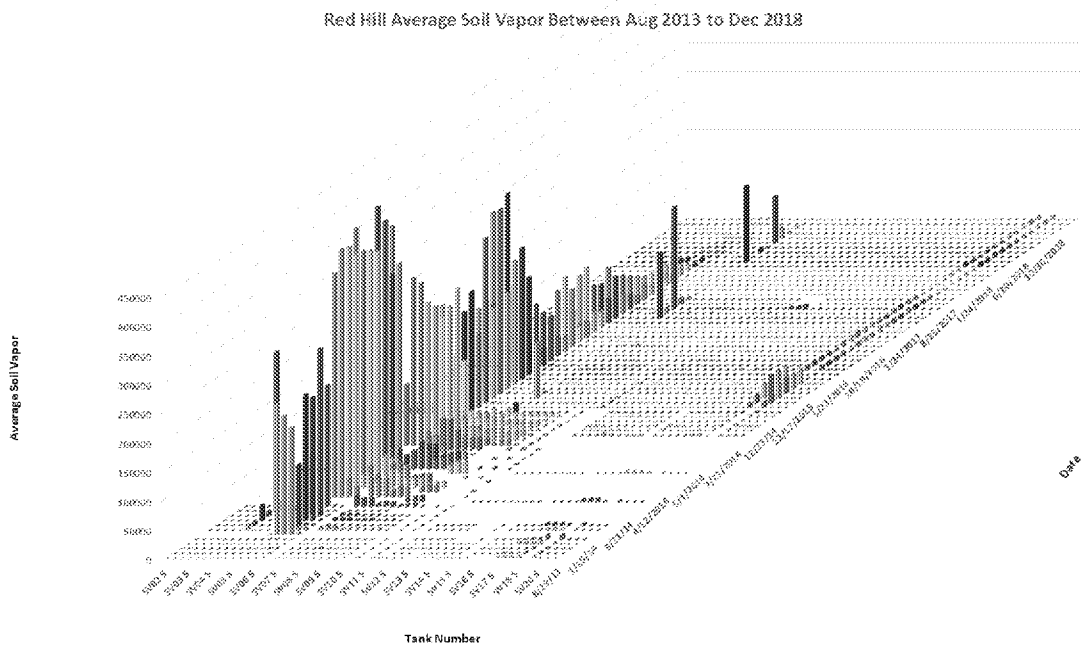


Figure 4. Waterfall plot of Red Hill vapor data from August, 2013, to December, 2018 with vertical axis as a linear scale.

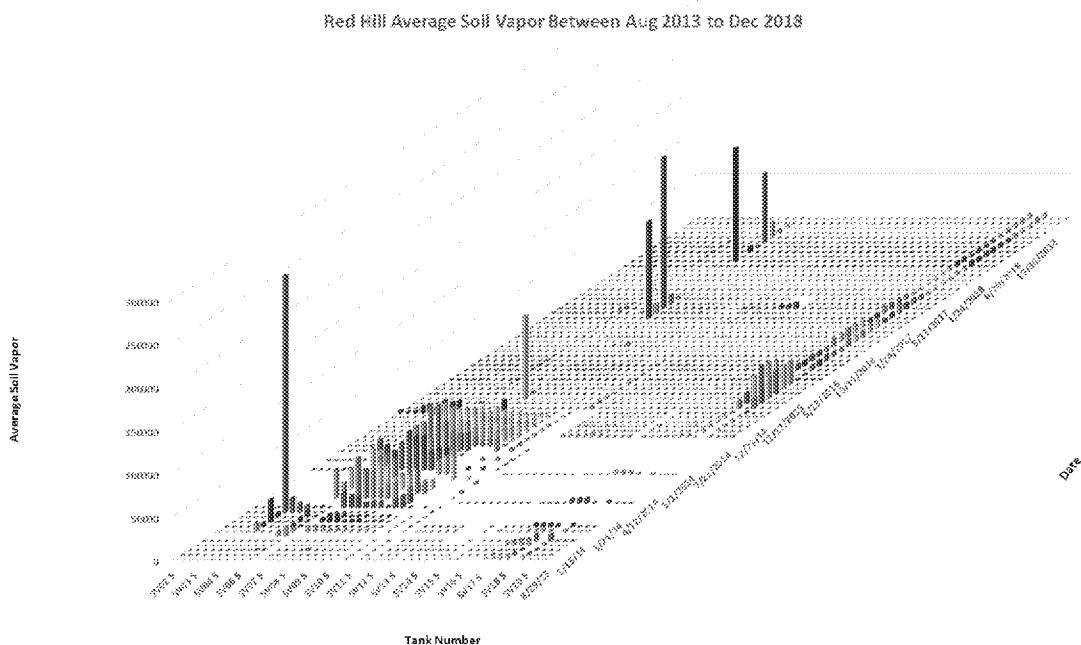


Figure 5. Waterfall plot of Red Hill vapor data without Tank 5 probes. The impact of the release at Tank 5 on vapor values at the probes for the surrounding tanks is evident.

Figure 6. A heatmap of the entire set of Red Hill soil vapor data from March, 2008, through April, 2020. Although not readable at this scale, each colored cell contains a vapor concentration value; the color scheme has red associated with the highest concentrations of organic vapor; yellow is intermediate, and green is lower vapor concentrations. The dark vertical lines separate the set of three probes for each of the tanks; the color coding is for the values within each set of three probes. The earlier data is at the top and become more recent downward; the lower numbered tanks are on the left and progress to higher tank numbers on the right. Cells without color are dates or probes for which data was not collected on the date plotted.



Figure 7. Heatmap for vapor concentration data recovered beginning in May, 2013 through April of 2020.

